

PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Polyethylene Elastomer

We, ESSO RESEARCH AND ENGINEERING COMPANY, a Corporation duly organised and existing under the laws of the State of Delaware, United States of America, of Elizabeth, New Jersey, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to the preparation of elastomeric halogenated polyethylene and in particular relates to the preparation of elastomeric halogenated polyethylene which is curable with conventional curing agents.

The preparation of synthetic rubber by curing chloro-sulfonated polyethylene is known to the art. However, chloro-sulfonated polyethylene is saturated and contains both $\text{—SO}_2\text{Cl}$ and —Cl groups attached to the hydrocarbon chains. Curing is effected through the $\text{—SO}_2\text{Cl}$ groups since most of the —Cl groups are located on secondary carbon atoms and therefore have a low order of reactivity. Elastomeric chlorinated polyethylenes are known to the art but they contain little unsaturation and the chlorine atoms contained therein are insufficiently labile for effective curing. However, other chlorinated polyethylenes which are also unsaturated are known to the art, but these materials are not rubbery, and while they can be cured, the products obtained are in the range of flexible leathery materials to hard plastics. No elastomeric halogenated polyethylene which can be cured with conventional curing agents to producing synthetic rubber is known to the art.

It has now been found that halogenating polyethylene having for instance a molecular weight in the range of 50,000 to 5,000,000 and a density in the range of 0.92 to 0.96 in an aromatic diluent under certain conditions produces an elastomeric halogenated polyethylene curable to a synthetic rubber. The halogenated polyethylene prepared according

to this invention has (1) sufficient unsaturation to be curable with sulfur, (2) labile halogen atoms attached directly to polymer carbon atoms through which it can also be cured with curing agents such as metal salts and difunctional compounds such as diamines, and (3) a sufficient number of halogen atoms that it contains substantially no residual crystallinity. The synthetic rubber produced has very good ozone resistance, tensile properties, and resiliency.

To this end, the invention provides the process for preparing elastomeric polyethylene, comprising the steps of (1) dissolving polyethylene in an inert aromatic diluent, (2) introducing a halogenating agent consisting of or containing chlorine or bromine, into the resultant solution at a temperature in the range $60\text{—}170^\circ\text{C}$. to produce a halogenated polyethylene containing from 25 to 65 wt. % of halogen, and having sufficient unsaturation to be cured by sulfur and sufficient halogen so that there is substantially no residual crystallinity.

The elastomeric halogenated polyethylene prepared by the novel process of the invention must contain sufficient unsaturation to be easily cured by sulfur and sufficient halogen to substantially entirely disrupt polyethylene crystallinity as determined by x-ray studies so that essentially no residual crystallinity remains in the halogenated polyethylene. The residual unsaturation is usually in the range of 0.3 to 6.0, particularly 1.0 to 3.0 mole %. The x-ray diffraction must record less than 5% crystallinity, preferably less than 1%. The quantity of halogen introduced into the polyethylene sufficient to substantially completely disrupt crystallinity depends on the halogen introduced. When the halogen is chlorine, the chlorine content is in the range of 25 to 65 wt. %, preferably from 27 to 35 wt. % and when bromine is introduced, the halogenated polyethylene contains from about 40 to 60 wt. % bromine, preferably from 45 to 55 wt. %.

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The molecular weight of the elastomeric halogenated polyethylene is in the range of about 20,000 to 1,000,000. It must be understood that the quantity of halogen introduced into the polyethylene to substantially completely disrupt crystallinity depends on the particular polyethylene chosen for the halogenation process. For example, the so-called "high pressure" polyethylene will require slightly less halogen than the more linear so-called "low pressure" polyethylenes, such as those developed by Ziegler, Standard of Indiana, and Phillips. When the term "substantially no residual crystallinity" is used in the specification and claims it is to be understood to refer to a crystallinity of less than 5% as determined by the x-ray diffraction method. The halogenated elastomeric polyethylene of the invention may be prepared by dissolving or slurrying the polyethylene in an aromatic diluent and introducing the halogenating agent into the resultant solution or slurry under conditions adapted to produce elastomeric halogenated polyethylene having the above stated properties.

The aromatic hydrocarbon diluent for the halogenation reaction must be one which is substantially inert, i.e. unreactive to chlorine or bromine under the halogenation conditions and in which the resulting halogenated polyethylene is soluble. Aromatic diluents such as benzene, chlorobenzene, and polychlorobenzene are particularly suitable for use in the present invention with chlorobenzene preferred. However, other aromatic diluents can be utilized such as fluorobenzene, bromobenzene, benzo-trifluoride and nitrobenzene.

The temperature of chlorination sufficient to produce the elastomeric halogenated polyethylene will depend on the halogen being introduced and on the activity of the halogenating agent. It must be high enough to obtain the desired degree of unsaturation and percent halogen content and low enough to prevent undesirable side reactions such as cross-linking and substantial breakdown. For chlorine introduction, the temperature is generally in the range of about 60 to 170° C., preferably 80 to 120° C. For bromine introduction, the temperature is generally in the range of 60 to 130° C., preferably 70 to 110° C. The halogenating agents which attach halogen atoms directly to polymer carbon atoms are chlorine, bromine, dichloro dimethylhydantoin, N-bromosuccinimide and the like with chlorine preferred. Sulfochlorinating agents such as SO_2Cl_2 and agents such as phosgene which attach $-\text{COCl}$ groups to the polymer carbon atoms are not useful in the present invention. Reaction times are from about one minute to one hour, and the particular time chosen will depend on the temperature of halogenation, the halogenating agent employed, the concentration of polymer and the concentration of halogenating agent. Pressures of from at-

mospheric to about 25 atmospheres can be used. However, pressures above atmospheric are required only when the desired halogenation temperature exceeds the boiling point of the solution at atmospheric pressure. The use of ultraviolet light in the process of this invention is not necessary. Halogenation rates are sufficiently rapid in the absence of ultraviolet light. Additionally, when ultraviolet light is used in the chlorination of polyethylene which is slurried in the aromatic diluent, a resinous product is obtained rather than a rubber. In general, the quantity of halogenating agent is chosen to produce from about 2 to 10 times the amount of halogen that reacts with the polyethylene. The halogenating agent can be added all at once at the beginning of the reaction but preferably it is added continuously or intermittently during the course of the reaction.

The halogenated polyethylene is isolated from the halogenation reaction mixture by precipitating it by the addition of from 0.5 to 5, preferably from 1 to 2 volumes of an alcohol or a ketone to the reaction mixture (based on the volume of reaction mixture). The alcohol is chosen from aliphatic alcohols having from 1 to 4 carbon atoms per molecule and is preferably methanol; and the ketone is chosen from ketones containing from 3 to 8 carbon atoms per molecule, and is preferably acetone.

Alternatively, the halogenated polyethylene can be isolated by washing the reaction mixture with water followed by removal of most of the diluent by steam stripping. With this technique, from 1 to 5 volumes of water based on the volume of reaction mixture is used to wash the reaction mixture and thereafter the inert aromatic diluent is steam stripped off, leaving the halogenated polyethylene as a slurry in water. The slurry is then filtered, and the precipitated product dried in conventional drying equipment, such as tunnel driers, tray driers, and degassing dewatering extruders.

A preferred process for obtaining the elastomeric halogenated polyethylene of the invention comprises the steps of (1) carrying out the polymerization of ethylene in contact with a low-pressure polymerization catalyst in an aromatic diluent, (2) preferably inactivating or removing the polymerization catalyst, (3) treating the polymerization mixture with a halogenating agent, and (4) isolating the resulting halogenated polyethylene. When this technique is used, a low-pressure polymerization catalyst is chosen to produce polyethylene having a molecular weight in the range of 50,000 to 5,000,000, preferably 100,000 to 1,000,000 and a density in the range of 0.92 to 0.96. Any low-pressure polymerization catalyst which yields polyethylene having these characteristics in the aromatic diluents of the invention can be used in this preferred pro-

cess. A mixture of a reducible heavy transition metal compound of Group IVA, VA, VIA, or VIII and an organo-metallic compound of a metal of Groups II or III can be employed, such as for example $\text{TiCl}_4 + \text{AlEt}_3$. The proportions of reducible heavy transition metal compound to organo-metallic compound are chosen to give polyethylene of the required molecular weight and density. Generally from 0.1 to 3 moles of reducible heavy metal compound is used per mole of organo-metallic compound. The reducible transition metal compound is preferably a titanium or zirconium halide such as titanium tri- or tetrachloride. The organo-metallic compound is preferably an aluminum alkyl such as triethyl aluminum and diethylaluminum chloride. The invention does not lie in the particular catalyst employed and any catalyst which produces the desired polyethylene can be used. Many catalyst combinations which will produce the desired polyethylene are known to the art.

The polymerization of ethylene in an inert aromatic diluent can advantageously be carried out by using one of the above catalyst mixtures at temperatures ranging from about 0 to 110° C. and at pressures ranging from atmospheric to about 15 atmospheres. The polymerization is permitted to proceed until the concentration of polyethylene in the aromatic diluent is from about 10 to 180 grams per liter.

The polymerization reaction mixture obtained by the above polymerization process or by another process is then utilized for the halogenation step without isolating the polyethylene contained therein. Unreacted olefins can be purged prior to halogenation by passing an inert gas such as nitrogen through the reaction mixture. It is then highly preferred to inactivate or physically remove the catalyst. The halogenation step can be carried out without inactivating or removing the catalyst but in general low halogenation reaction rates and a gelled halogenation product result. The catalyst can be removed by physical removal such as filtration if the catalyst is insoluble in the aromatic diluent. Alternatively, the catalyst can be removed by treating the reaction mixture with about an equal volume of water with stirring, allowing the resulting mixture to settle in a water layer and in an inert solvent layer, and removing the water layer. This water treatment is repeated until a large part of the polymerization catalyst is removed from the reaction mixture. Alternatively and preferably, a catalyst inactivator can be added to the reaction mixture in amounts ranging from 1 to 30 times the amount necessary for inactivation. The inactivated catalyst is thereafter allowed to remain in the reaction mixture. The catalyst inactivator can be chosen with a boiling point below the halogenation temperature to allow for easy removal, although removal of excess catalyst inactivator is usually unnecessary. When the catalyst is a mixture of a reducible transition metal compound and an organo-metallic compound, the catalyst inactivator is a compound containing an OH group, such as steam, water and lower aliphatic alcohols having from 1 to 5 carbon atoms per molecule, preferably methanol; or a chelating agent, such as ketones and 2,3- and 2,4-diketones. Water and steam are preferred. A mixture of any of the above catalyst inactivators can also be used. When the term "inactivate" is used henceforth in the specification and claims it is to be understood to include physical removal. The above mixture containing polyethylene is then used in the halogenation reaction as above described.

After the halogenation step the halogenated polyethylene can be isolated by any convenient procedure such as those given above. However, another isolation technique for isolating the halogenated polyethylene can be employed and is preferred where inactivated catalyst is allowed to remain in the aromatic diluent during the halogenation step. This technique involves the addition of a small quantity i.e. from 1 to 8 mole of catalyst of a chelating agent such as acetylacetone to solubilize the catalyst residues. Thereafter a C_1 to C_4 aliphatic alcohol is added to precipitate the halogenated polyethylene substantially free of catalyst residues.

The isolated elastomeric halogenated polyethylene can then be cured with conventional curing agents, such as sulfur-zinc oxide mixtures to form synthetic rubbers having good to excellent mechanical, dynamic and chemical properties. Since the halogenated polyethylene of the invention contains both unsaturation and relatively active chlorine groups, a combination of (1) a curing agent which cures through halogen groups and (2) a curing agent which cures through unsaturation is used. Alternatively, free radical producing substances can be used alone, such as dicumyl peroxide or 2,5-bis(tert-butylperoxy) - 2,5-dimethylhexane. Also, combinations of free radical producing substances with either a curing agent which cures through halogen groups or a curing agent which cures through unsaturation, or both can be used. For example, dicumyl peroxide plus sulfur or zinc oxide or both can be used. From 0.5 to 15, preferably from 2 to 8 parts by weight of the halogen group-curing agent is used per 100 parts of halogenated polyethylene and from 0.5 to 10 parts, preferably from 1 to 7 parts by weight of the unsaturation-curing agent is used per 100 parts of halogenated polyethylene except when dimethylol phenol resins are used as the unsaturation-curing agents. When these resins are used, they are used in the proportion of from 5 to 15 parts by weight per 100 parts of halogenated polyethylene. Curing agents adapted to cure through halogen groups include metal oxides, metal salts, metal powders

amines and polyamines. In general, the metal components of the metal salts, metal oxides and metal powders are chosen from Groups IIA and IIB of the Periodic Table and copper and iron. Particularly useful are the metal oxides, sulfides, nitrates, phosphates, sulfates, and organic acid salts of zinc, cadmium, manganese, iron and lead. When amines and polyamines are used in the curing mixture, they are chosen from any diamine, triamine and high polyamine having one or more of the following types of amino groups. (a) substituted amino groups, (b) monosubstituted amino groups, (c) disubstituted amino groups, and (d) heterocyclic amino groups such as pyridine. The substituents on the mono- and di-substituted amino groups are one or more alkyl, aryl, and heterocyclic groups.

The components of the curing mixture useful for curing through unsaturation include sulfur, resins such as dimethylol phenol resins and halogenated dimethylol phenol resins, and quinone dioxime and its derivatives. Either the halogen group-curing agent or the unsaturation-curing agent can be used alone to effect partial curing, and this is within the broader scope of the invention, but the use of either type of curing agent is not to be considered as equivalent to the use of a combination of these curing agents, since in general much poorer properties are obtained for the synthetic rubbers when only one type of curing agent is used.

When dicumyl peroxide is used as the curing agent, from 0.1 to 10 parts by weight, preferably 0.5 to 4.0 parts by weight per 100 parts of chlorinated polymer is employed.

Inert fillers such as carbon blacks, silica, mica and others of like nature can be added to the curing mixtures in amounts of from 5 to 150 parts by weight, preferably about 50 parts per 100 parts of halogenated polymer. Any type of carbon black can be used, such as channel blacks, furnace blacks, acetylene blacks, lamp blacks, and the like. However, when dicumyl peroxide is used as a curing agent a neutral or basic carbon black is required such as the furnace blacks.

A small quantity, i.e. from 0.1 to 8%, preferably from 0.5 to 3% of a conventional rubber accelerator, for example tetramethylthiuram disulfide, benzothiazyl mono- and disulfide, 2-mercapto-benzothiazole, N-cyclohexylbenzothiazole-2-sulfenamide, selenium diethyl dithiocarbamate disulfide, and zinc butylxanthate can also be added with the filler. Mixtures of rubber accelerators can also be used. Additionally, antioxidants can be added when desired, such as for example secondary aromatic amines and phenols, e.g., phenyl-beta-naphthylamine, N,N'-di-beta-naphthyl-p-phenylene-diamines, aldol - alpha - naphthylamine, 2,2,4-trimethyl-1,2-dihydroquinoline, hydroquinone monobenzyl ether, and 2,2'-methylene-bis (4-methyl-6-tert. butylphenol).

From 0.01 to 10%, preferably 0.1 to 2% of antioxidant can be used. When quinone dioxime or its derivatives are used, it is advantageous to include from 5 to 15 parts by weight of an oxidizing agent such as red lead in the curing mixture rather than an antioxidant. It should be noted that all antioxidants cannot be used with dicumyl peroxide. However, certain antioxidants, such as hydroquinone monobenzyl ether that do not react rapidly with dicumyl peroxide at curing temperatures can be employed.

Oils derived from coal tar, pine tar and/or petroleum can be added to the curing mixture if desired and from 2 to 30 parts preferably 5 to 15 parts by weight of oil per 100 parts of chlorinated polymer can be employed to serve as extenders, softening agents or tackifying agents.

The reaction between the halogenated polyethylene and the curing agent is carried out by mixing the chlorinated polymer and the curing agent on a rubber mill and heating the resulting mixture in a standard rubber press in the range of from 225° F. to 350° F., preferably 280° F. to 315° F. and more preferably about 310° F. until curing is effected. Fillers, rubber accelerators and antioxidants are added with the curing agent mixture as desired. The mixing is carried out on a rubber mill followed by heating the resulting mixture to reaction temperature in a standard rubber press or other conventional rubber curing equipment. The mixing can also be carried out in other rubber compounding equipment, such as Banbury mixers and kneaders.

The cured halogenated polyethylene of the invention has outstanding tensile properties, good dynamic properties at temperatures between 0° to 70° C., and excellent ozone resistance. They are useful wherever a good general purpose elastomer is required, such as motor mounts, hoses, gaskets and the like. These polymers are useful in applications where chemical inertness, solvent resistance and stability is required.

The invention will be understood more clearly from the following Examples, wherein it is to be understood that the term "Examples" includes embodiments not according to the invention, but which are included for comparative purposes.

EXAMPLES 1 TO 11.

Polyethylene, which had been prepared with an $AlEt_2Cl/TiCl_4$ catalyst and which had the properties shown in Table I, was dissolved in chlorobenzene to a concentration of 50 g./l. at a temperature of 110°-120° C. Chlorine gas was bubbled through the hot solution until the desired amount of chlorine had been introduced. After chlorination, the chlorinated polyethylene was isolated by precipitation with isopropyl alcohol (one liter of isopropyl alcohol per liter of solution). The precipitated chlorinated polyethylene was washed several times

with isopropyl alcohol in a Waring blender, filtered and then dried in a vacuum oven at 50–60° C.

Full details on the chlorination and the properties of the chlorinated polyethylenes are given in Table I. 5

TABLE I
Chlorination of Polyethylene of Molecular Weight 150,000 (m) in Chlorobenzene Solution at Elevated Temperatures (110–120° C.)

Example	Starting Polymer	1	2	3	4	5
Chlorination						
Diluent		Chlorobenzene				
Volume, ml.	1000	1000	1000	1000	3000	1000
Polyethylene, g.	50	50	50	50	150	50
Gel Point, °C. (i)	@100	ca. 40	None	None	—	—
U.V. Light (k)	—	No	No	No	No	Yes
Temperature, °C.	—	117–118	110–120	120–122	118–122	114–115
Time of Reaction, Min.	—	15	45	30	25	30
Cl ₂ Used, g.	—	20	66	42	161	47
Product, g.	—	59.5	60.8	64.6	194	64.3
Properties of Product						
Inherent Viscosity, dl./g. (a)	2.40	2.13 (i)	1.48	1.48	(i)	1.28
% Solubles (b)	—	3	100	100	86	100
Iodine Number, cg. I ₂ /g. Polymer (l)	—	—	—	—	—	3.33
Mole %, Unsaturation (c)	ca. 0.1	—	—	—	—	3.3
Weight %, Chlorine (d)	0	13.0	22.3	23.2	25.7	28.0
Crystallinity (e)	Very High	High	Low	Low	—	—
Tensile Strength, psi (f)	4310	3040	3780	2680	880	1270
Elongation, % (f)	755	760	780	740	260	980
Apparent Modulus of Elasticity, psi × 10 ⁻⁵ (g)						
At 25° C.	1.09	0.19	0.16	0.11	—	—
0° C.	1.59	0.35	0.16	0.11	—	—
–25° C.	2.70	0.95	0.54	0.30	0.20	0.19
–50° C.	4.76	2.28	1.48	1.38	1.17	1.41
Density, g./cc. (h)	(0.946)	(0.993)	1.044	(1.047)	(1.067)	1.073

TABLE I (Continued)

Example	6	7	8	9	10	11
Chlorination						
Diluent			Chlorobenzene			
Volume, ml.	3000	1000	1000	1000	1000	1000
Polyethylene, g.	150	50	50	50	50	50
Gel Point, °C. (i)	—	—	None	None	—	None
U.V. Light (k)	No	No	No	No	No	No
Temperature °C	101—116	111—115	110—116	118—121	108—122	117—122
Time of Reaction, Min.	120	60	60	75	90	105
Cl ₂ Used, g.	640.5	—	99	126	138	149
Product, g.	157	67.7	71.5	73.8	87.7	97.2
Properties of Product						
Inherent Viscosity, dl./g. (a)	1.27	0.88	1.02	0.73 (i)	0.14 (i)	0.79
% Solubles (b)	74	100	100	94	52	100
Iodine Number, cg. I ₂ /g. Polymer (1)	2.85	0.61	0.25	3.87	0.83	—
Mole %, Unsaturation (c)	3.0	0.67	0.27	4.5	0.95	—
Weight %, Chlorine (d)	30.0	34.5	34.9	38.4	39.8	45.8
Crystallinity (e)	—	—	None	None	None	None
Tensile Strength, psi (f)	—	1130	230	1190	—	600
Elongation, % (f)	—	240	>1000	>1000	—	600
Apparent Modulus of Elasticity, psi × 10 ⁻⁵ (g)	—	—	—	—	—	—
At 25° C.	—	—	—	—	—	—
0° C.	—	—	—	—	—	—
-25° C.	—	0.12	0.26	0.48	—	0.50
-50° C.	—	0.93	1.70	1.68	—	2.33
Density, g./cc. (h)	—	(1.132)	(1.147)	(1.161)	—	2.86
						(1.284)

- (a) In tetralin at 125° C. at a concentration of 1 g./l.
- (b) Determined from a toluene solution viscosity at 25° C. at a concentration of 1 g./l.
- (c) Assuming chlorinated polyethylene is a copolymer of vinyl chloride and ethylene.
Calculated from the expression
$$\text{Mole } \%, \text{ Unsaturation} = \frac{[\text{moles } I_2] (2/3) (100\%)}{\text{moles vinyl chloride} + \text{moles ethylene}}$$
- (d) Dietert method.
- (e) Via x-ray analysis.
- (f) ASTM D 412.
- (g) ASTM D 1043.
- (h) By titration.
- (i) Not completely soluble in tetralin at 125° C. at a concentration of 1 g./l.
- (j) Temperature at which the polymer begins to precipitate from solution.
- (k) From a 200 Watt Westinghouse Sun Lamp.
- (l) In CCl₄ at 25° C. with I₂.
- (m) Molecular weight calculated from the Inherent Viscosity by means of the "Harris" correlation. (Journ of Polymer Science No. 8 page 361—1952).

It can be seen from the above table that chlorinated polyethylenes were obtained which contained from 13.0 to 45.8% chlorine by weight. The polymers containing 23.2% or less chlorine still contained some crystallinity as determined by x-ray analysis and were not according to the invention. Those containing above 34.5% chlorine were amorphous by x-rays. Although no x-ray data were obtained on chlorinated polyethylene containing between 23.2% chlorine and 34.5% chlorine, data obtained on the vulcanizate properties showed that the chlorinated polyethylenes behaved as rubbers only when they contained at least 27% chlorine.

The chlorinated polyethylenes contained unsaturation appreciably greater than the starting polyethylene, as shown from iodine numbers on these polymers. If the chlorinated polyethylene is assumed to be a copolymer of vinyl chloride and ethylene, then chlorinated polyethylenes were obtained having as much as

4.5 mole % unsaturation.

The densities of the chlorinated polyethylenes increased linearly with increasing chlorine content. Both the tensile properties and the apparent moduli of elasticity of the chlorinated polyethylenes showed a minimum between chlorine levels of 25% and 35%.

The chlorinated polyethylenes containing more than 27% chlorine are normally white, rubbery products which are rather easily handled on rubber mills.

These examples show that rubbery, amorphous, substantially non-cross-linked polyethylenes containing unsaturation appreciably higher than the starting polyethylene can be obtained by chlorination in halogenated diluents at temperatures of 110—125° C.

EXAMPLE 12.

The rubbery chlorinated polyethylenes obtained in Examples 5, 6, 7, and 8 were compounded on a cool rubber mill according to Recipe A.

Recipe A	
Ingredient	Parts by Weight
Polymer	100
Sulfur	2
Tetramethylthiuram Disulfide	1
Benzothiazyl Disulfide	1
Zinc Oxide	5

The compounded stocks were cured at 250° of the gum vulcanizates are given in Table 5
280° F., and 308° F. The tensile properties II.

Example	TABLE II*			
	5	7	6	8
Chlorine Content, Wt. %	28.0	34.5	30.0	34.9
Curing Temperature, °F.	250	250	250	—
Curing Time, Min.	15	45	15	—
Tensile Strength, psi.	2200	3900	3100	—
Elongation, %	1110	670	550	—
300% Modulus, psi.	130	440	420	—
Curing Temperature, °F.	280	280	280	280
Curing Time, Min.	30	30	30	30
Tensile Strength, psi.	4410	830	610	4060
Elongation, %	720	150	130	630
300% Modulus, psi.	180	—	—	154
Curing Temperature, °F.	308	308	308	308
Curing Time, Min.	45	30	45	15
Tensile Strength, psi.	880	670	Over	1220
Elongation, %	170	90	Cured	240
300% Modulus, psi.	—	—	—	—

* Data obtained on microdumbbells — ASTM D 412.

The tensile properties data given in Table II show that chlorinated polyethylenes prepared according to the process of this invention are readily cured with conventional rubber recipes to vulcanizates with outstanding tensile properties. Curing temperatures as low as 250° F. are very effective. Gum vulcanizates

with tensile strengths of 4000 psi and greater are readily obtained.

EXAMPLE 13.

The rubbery chlorinated polyethylenes of Examples 8, 9, 10, and 11 were compounded on a cool rubber mill according to the following recipes.

Recipe B

Ingredients	Parts by Weight
Polymer	100
Semi-Reinforcing Furnace Black	50
m-Phenylenediamine	3

Recipe C:

Polymer	100
Semi-Reinforcing Furnace Black	50
Zinc Oxide	5

Recipe D:

Polymer	100
Semi-Reinforcing Furnace Black	50
Sulfur	2
Tetramethylthiuram Disulfide	1
Benzothiazyl Disulfide	1

Recipe E:

Polymer	100
Semi-Reinforcing Furnace Black	50
Sulfur	2
Tetramethylthiuram Disulfide	1
Benzothiazyl Disulfide	1
Zinc Oxide	5

The compounded stocks were press cured 15 minutes and 30 minutes at 280° F. and 45 minutes at 308° F. The tensile properties of

the reinforced filter vulcanizates are given in Table III.

TABLE III*

Example	8			9		
Wt. % Chlorine	34.9			38.4		
Recipe B						
Cure Conditions	30'/280°F.	15'/308°F.	45'/308°F.	30'/280°F.	15'/308°F.	45'/308°F.
Tensile Strength, psi	—	1690	2690	3360	3400	3280
Elongation, %	—	510	395	270	250	210
300% Modulus, psi	—	940	2360	—	—	—
Recipe C						
Cure Conditions	30'/280°F.	15'/308°F.	45'/308°F.	30'/280°F.	15'/308°F.	45'/308°F.
Tensile Strength, psi	560	620	900	2480	3240	1780
Elongation, %	>1000	>1000	860	380	290	40
300% Modulus, psi	—	—	570	2200	—	—
Recipe D						
Cure Conditions	30'/280°F.	15'/308°F.	45'/308°F.	30'/280°F.	15'/308°F.	45'/308°F.
Tensile Strength, psi	140	150	750	2160	2730	3050
Elongation, %	>1000	>1000	>1000	620	520	390
300% Modulus, psi	—	—	—	1060	1760	2740
Recipe E						
Cure Conditions	30'/280°F.	15'/308°F.	45'/308°F.	30'/280°F.	15'/308°F.	45'/308°F.
Tensile Strength, psi	2760	2610	2520	3100	3050	2950
Elongation, %	520	480	80	220	100	60
300% Modulus, psi	1820	2030	—	—	—	—

* Data obtained on microdumbbells — ASTM D 412.

TABLE III* (Continued)

Example	10			11		
Wt. % Chlorine	39.8			45.8		
Recipe B						
Cure Conditions	30'/280°F.	15'/308°F.	45'/308°F.	30'/280°F.	15'/308°F.	45'/308°F.
Tensile Strength, psi	2090	2120	2820	2160	2360	2730
Elongation, %	490	430	320	290	255	210
300% Modulus, psi	1550	1750	2750	—	—	—
Recipe C						
Cure Conditions	30'/280°F.	15'/308°F.	45'/308°F.	30'/280°F.	15'/308°F.	45'/308°F.
Tensile Strength, psi	1570	1660	1650	2280	1440	1930
Elongation, %	485	420	405	350	130	150
300% Modulus, psi	1140	1320	1510	2160	—	—
Recipe D						
Cure Conditions	30'/280°F.	45'/308°F.	30'/280°F.	15'/308°F.	15'/308°F.	45'/308°F.
Tensile Strength, psi	1530	1625	1980	1960	1710	1520
Elongation, %	920	890	705	380	350	215
300% Modulus, psi	600	655	990	1570	1580	—
Recipe E						
Cure Conditions	30'/280°F.	15'/308°F.	45'/308°F.	30'/280°F.	15'/308°F.	45'/308°F.
Tensile Strength, psi	3100	2780	2810	2380	2480	3030
Elongation, %	390	110	60	320	120	50
300% Modulus, psi	2750	—	—	2280	—	—

* Data obtained on microdumbbells — ASTM D 412.

It can be seen from Table III that the chlorinated polyethylenes prepared according to the process of this invention can be cured with zinc oxide alone, with sulfur-accelerators alone or with the combination. Furthermore, it can be seen that these polymers are readily

cured with *m*-phenylenediamine. This shows that these chlorinated polyethylenes possess both unsaturation and labile chlorine and that they can be cured through either or both. This table further shows that reinforced filler vulcanizates of chlorinated polyethylenes have very

good tensile properties and that curing temperatures of 280° F. to 380° F. are very effective.

Ozone tests were conducted on samples of the above vulcanizates, and the data therefor are given in Table IV.

TABLE IV

Ozone Resistance Properties

Example	8	9	10	11
Wt. % Chlorine	34.9	38.4	39.8	45.8
Recipe	E	E	E	B
Cure Conditions	30'/280°F.	30'/280°F.	15'/308°F.	30'/280°F.
Tensile Properties Before Ozone Test				
Tensile Strength, psi	2760	3100	3100	2120
Elongation, %	520	220	390	430
300 Modulus, psi	1820	—	2750	1750
Ozone Test (a)				
Time to Crack, Min.	193	74	>300	>300
Time to Break, Min.	255	77	>300	>300
Tensile Properties After Ozone Test				
Tensile Strength, psi	—	—	2805	2500
Elongation, %	—	—	295	310
			2190	1740
			380	305

(a) Microdumbbells at 50% extension in an 0.2 volume % ozone atmosphere.

It can be seen from Table IV that the reinforced filler vulcanizates of these chlorinated polyethylenes have excellent ozone resistance.

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EXAMPLE 14.

The chlorinated polyethylene of Example 4 was loaded with varying amounts of a fine Thermal Black and cured according to Recipe

A. Tensile properties data on the loaded vulcanizates are given in Table V.

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TABLE V*

FT, Black, phr	0	10	20	30	40	50	75	100
Cure								
15'/250° F.								
Tensile Strength, psi	3100	4200	3730	3240	2960	2617	1680	1720
Elongation, %	550	600	580	540	550	590	320	300
300% Modulus, psi	420	460	810	910	1200	1300	1660	1710
15'/280° F.								
Tensile Strength, psi	800	1380	1640	1840	1880	2260	1890	1820
Elongation, %	160	200	170	180	180	270	210	160
300% Modulus, psi	—	—	—	—	—	—	—	—
30'/280° F.								
Tensile Strength, psi	610	1520	1410	1700	1870	2090	2150	1970
Elongation, %	130	170	160	150	140	190	160	100
300% Modulus, psi	—	—	—	—	—	—	—	—

* Tensile properties determined on microdumbbells. ASTM D 412.

It can be seen from Table V that small amounts of black improved tensile properties generally. As the amount of black was increased the moduli increased, tensile strengths decreased and elongations decreased. However, reinforced filler vulcanizates with good tensile properties were obtained under proper curing conditions. A curing temperature of 250° F.

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was better than one of 280° F. which shows the rapidity of cure of the chlorinated polyethylenes even under conditions of high loading.

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at 80—90° C. at a concentration of 50 g./l. Chlorine gas was bubbled through the slurry in the presence of ultraviolet light until the desired amount of chlorine had been added. The products were isolated as in Examples 1 to 11. Data on the preparation and properties of the chlorinated polyethylenes are given in Table VI.

EXAMPLES 15 TO 19.

In these examples 50 g. of the polyethylene of Example 1 were slurried in chlorobenzene

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TABLE VI

Example	15	16	17	18	19	20	21	22
Chlorination								
Diluent	Chlorobenzene							
Volume, ml.	1000							
Polyethylene, g.	50							
U.V. Light (a)	Yes	Yes	Yes	Yes	Yes	No	No	No
Temperature, °C.	84-87	80-90	85-88	85-92	83-91	82-92	80-86	83-90
Time of Reaction, Min.	15	30	30	60	100	60	90	175
Cl ₂ Used, g.	25	48	49	99	151	98.5	140	—
Product, g.	58.1	60.3	70.0	75.0	106.8	50.0	53.0	88.0
Properties of Product								
Nature of Product	Resinous				Rubbery			
Inherent Viscosity, dl/g. (b)	2.04	2.03	1.78	1.87	1.31	1.73	0.98	0.60
% Solubles (c)	37	60	72	58	96	90	87	100
Weight %, Chlorine (d)	17.1	26.5	31.6	42.4	54.1	25.2	30.6	47.4
Density, g./cc. (e)	1.043	—	1.148	1.237	1.381	1.063	1.094	1.285
Apparent Modulus of Elasticity, psi × 10 ⁻⁵ (f)								
At 25° C.	—	—	—	—	—	—	—	—
0° C.	—	—	—	—	—	—	—	0.35
-25° C.	—	—	—	—	—	—	—	2.52
-50° C.	—	—	—	—	—	1.06	1.41	3.49

(a) Supplied by a 200 Watt Westinghouse Sun Lamp.

(b) In Tetralin at 125° C. at a concentration of 1 g./l.

(c) Determined from a toluene solution viscosity at 25° C. at a concentration of 1 g./l.

(d) Dietert determination.

(e) By titration.

(f) ASTM D 1043.

It can be seen from Table VI that the products obtained contained 17.1%, 26.5%, 31.6%, 42.4% and 54.1% chlorine by weight. All of these products were tough and horny and were not in the least rubbery even though four of these products contained sufficient chlorine to disrupt polyethylene crystallinity entirely.

These products were not cross-linked as evidenced by their complete solubility in tetralin at 125° C. at a concentration of 1 g./l. In fact, the product containing 54.1% chlorine was almost totally soluble in toluene (under the conditions of a toluene solution viscosity test, i.e. two days of room temperature tumbling of 1 g. of polymer per liter of toluene).

These examples show that whereas ultraviolet light accelerates chlorination and still gives rubbery products when the polyethylene is chlorinated in solution, ultraviolet light adversely affects the slurry chlorination of polyethylene. Although the products obtained are

not cross-linked, they are nevertheless not rubbers.

EXAMPLES 20 TO 22.

In these examples 50 g. of the polyethylene of Example 1 were slurried in chlorobenzene at 80–90° C. at a concentration of 50 g./l. Chlorine gas was bubbled through the slurry in the absence of ultraviolet light until the desired amount of chlorine had been added. The products were isolated as in Examples 1 to 11. Details of the chlorination and properties of the products obtained are also given in Table VI. It can be seen that the products obtained contained 25.2%, 30.6% and 47.4% chlorine, respectively, and all were rubbery.

The products from Examples 21 and 22 were compounded on a cool rubber mill according to Recipe A, and the compounded stocks were cured 30 minutes at 280° F. and 45 minutes at 309° C. The tensile properties of the gum vulcanizates are given in Table VII.

TABLE VII

Example	21		22	
Wt. % Chlorine	30.6		47.4	
Cure Conditions	30'/280°F.	45'/309°F.	30'/280°F.	45'/309°F.
Tensile Strength, psi.	3630	1120	2960	730
Elongation, %	800	160	320	50
300% Modulus, psi.	100	—	2280	—

It can be seen that the products prepared in chlorobenzene slurry in the absence of ultraviolet light are readily curable with sulfur-metal oxide recipes. Additionally, the tensile properties of the vulcanizates are outstanding. Also, Examples 15 through 22 show that rubbery, curable chlorinated polyethylenes can be prepared in aromatic diluents when the polyethylene is slurried but only in the absence of ultraviolet light. As was shown in Examples 15 through 19 resinous products only are produced in the presence of ultraviolet light.

EXAMPLE 23.

50 g. of polyethylene (prepared with an $\text{AlEt}_2\text{Cl}/\text{TiCl}_4$ catalyst) with an intrinsic viscosity of 4.7 was dissolved in o-dichlorobenzene at a temperature of 170° C. Over a period of 30 minutes, 55 g. of chlorine was bubbled through the hot solution at 168–174° C. After isolating the chlorinated polyethylene in the usual manner, it was found to contain 10.1% chlorine by weight. Full details on preparation and properties of this chlorin-

ated polyethylene are given in Table VIII.

This example shows the use of o-dichlorobenzene as a diluent in the preparation of chlorinated polyethylenes. It further illustrates the use of higher chlorinating temperatures, i.e. 165–175° C.

EXAMPLES 24 TO 29.

In these examples the higher molecular weight polyethylenes of Example 23 was dissolved in chlorobenzene at 110–120° C. at a concentration of 20 g./l. (except for Example 24 where the concentration was 15 g./l.). Chlorine was passed into the hot solutions in the absence of ultraviolet light until the desired amount of chlorine had been introduced. The products were isolated in the usual manner. Products containing 27.5%, 31.4%, 38.9%, 44.2%, 47.7% and 62.1% chlorine were obtained. All of the products were rubbery.

Full details on the preparation and properties of the products are given in Table VIII.

TABLE VIII
Chlorination of Polyethylene of Molecular Weight 420,000 in Solution at Elevated Temperatures
in the Absence of Ultraviolet Light

Example	23	24	25	26	27	28	29
Chlorination							
Diluent	O-Dichlorobenzene						
Volume, ml.	1000						
Polyethylene, g.	50	22.5	30	30	30	30	30
Chlorine Used, g.	55	53	59	89	126	124	200
Time of Reaction, Min.	30	30	31	45	60	90	120
Temperature, °C.	168-174	111-115	115-120	118-119	115-121	118-121	117-120
Product, g.	28	23	31.7	28	41.6	49.0	53.5
Properties of Product							
Chlorine Content, Wt. % (a)	10.1	27.5	31.4	38.9	44.2	47.7	62.1
Iodine Number, cc. I ₂ /g. Polymer (b)	—	—	5.58	—	—	—	—
Inherent Viscosity, dl./g.	3.48	1.98	2.01	1.51	1.82	0.85	1.41
% Solubles (d)	—	100	97	96	96	98	97
Density (e)	—	1.071	1.091	—	1.259	1.298	—
Apparent Modulus of Elasticity							
Psi × 10 ⁻⁶ (f)							
At 25° C.	—	—	—	—	—	—	—
0° C.	—	—	—	—	0.53	—	—
-25° C.	—	0.23	0.11	1.12	1.78	2.12	1.13
-50° C.	—	1.19	1.18	1.99	2.42	2.83	2.72

(a) Diertert determination.

(b) In CCl₄ at 25° C. with I₂.

(c) In tetralin at 125° C. at a concentration of 1 g./l.

(d) Determined from a toluene solution viscosity at 25° C. at a concentration of 1 g./l.

(e) By titration.

(f) ASTM D 1043.

The data of the above Table VIII illustrates the use of higher molecular weight polyethylenes in the synthesis of rubbery, curable chlorinated polyethylene. They further illus-

trate that rubbery products can be obtained with chlorine levels as high as 62.1% chlorine by weight.

The products in these examples were com-

pounded with Recipe A on a cool rubber mill 10 and cured. The tensile properties of the gum vulcanizates are given in Table IX.

TABLE IX*

Example	24	25	26	27
Wt. % Chlorine	27.5	31.4	38.9	44.2
Cure	30'/280°F.	30'/280°F.	15'/280°F.	15'/280°F.
Tensile Strength, psi	4320	3820	3250	3590
Elongation, %	660	580	780	460
300% Modulus, psi	300	170	110	350
Example	28	29		
Wt. % Chlorine	47.7	62.1		
Cure	30'/250°F.	20'/280°F.	30'/280°F.	20'/280°F.
Tensile Strength, psi	6190	4570	3870	3050
Elongation, %	310	190	160	510
300% Modulus, psi	5450	—	—	240

* Tensile properties obtained on microdumbbells. ASTM D 412.

As the data in Table IX show, gum vulcanizates with tensile strengths exceeding 6000 psi are obtainable. The cure temperature required varies with chlorine content but temperatures as low as 250° F. are adequate.

EXAMPLE 30.

In 3 liters of chlorobenzene were dissolved 45 g. of a polyethylene of molecular weight 1,200,000 at 110—120° C. Into the hot solution at 112—120° C. in the absence of ultraviolet light were passed 92 g. of chlorine over a period of 60 minutes. The product was worked up in the usual manner.

The chlorinated polyethylene was a rubbery, white product. It contained 30.7% chlorine by weight, an iodine number of 1.5 cg. I₂/g. polymer, a density of 1.093 g./cc. and an apparent modulus of elasticity at -50° C.

of 116,000 psi.

This example illustrates that starting polyethylenes with molecular weights over one million can be used according to the process of this invention to produce rubbery, curable chlorinated polyethylenes.

EXAMPLE 31.

The chlorinated polyethylenes from Examples 6, 8, 25, 26 and 28 were compounded according to Recipe A and cured 20 minutes at 280° F. A natural rubber (smoked sheet) vulcanizate control was also obtained for comparison purposes. The resilience of these polymer vulcanizates was measured with a Goodyear-Healy rebound pendulum at room temperature. The % rebounds and hardness of the vulcanizates were as follows:

Example	Wt. % Chlorine	% Rebound	Shore Hardness
6	30.0	70.6	55
7	34.9	68.9	—
24	27.5	75	50
27	44.2	75	54
29	30.7	81	54
Natural Rubber	—	76	32

This illustrates that chlorinated polyethylene gum vulcanizates can be even more resilient than those of natural rubber and are generally harder than those of natural rubber.

Using a Goodyear-Healy rebound pendulum

the effect of temperature on the resilience of the gum vulcanizate of the chlorinated polyethylene from Example 8 was determined. A natural rubber gum vulcanizate control was made. The results were as follows:

Natural Rubber		Chlorinated Polyethylene of Example 8	
Temp., °C.	% Rebound	Temp., °C.	% Rebound
-57	17.2	-37	30.3
-44	16.9	-15	30.3
-35	19.4	0	45.6
-26	37.3	10	56.4
-13	62.5	20	65.7
0	68.1	24	68.1
25	75.8	27	68.9
34	75.8	30	70.6
45	76.6	45	68.9
50	77.5	61	66.5
60	78.4	81	66.5
75	79.3	100	64.8
88	80.2		
100	81.0		

These data show an interesting unique property for chlorinated polyethylenes prepared according to the process of this invention. Whereas natural and synthetic rubbers have increasing resiliency with increasing temperature, chlorinated polyethylene exhibits the phenomenon of decreasing resiliency with in-

creasing temperature. The reason for this, as shown in the following example, is that the internal viscosity of the system increases with increasing temperature. Since relative damping (which is related to resiliency) is related to the dynamic modulus (K) and the internal viscosity (ηf) according to the expression

$$\frac{1}{\text{Resiliency}} \propto \text{Relative Damping} = 200; \frac{1 + K}{4\eta f}$$

it follows that an increase in ηf will mean a decrease in resiliency.

EXAMPLE 32.

A gum vulcanizate of the chlorinated polyethylene from Example 30 was obtained according to Recipe A and curing 20 minutes

at 280° F. A natural rubber gum vulcanizate was made also for purposes of comparison.

The dynamic properties of this chlorinated polyethylene and natural rubber were obtained at various temperatures by means of a modified Yerzley Oscillograph. The results are given in Table X.

TABLE X

Effect of Temperature on Dynamic Properties of Chlorinated Polyethylene
(Example 30) and Natural Rubber Gum Vulcanizates

Dynamic Modulus (K) (Megadynes/cm ²)	Natural Rubber (a)	Chlorinated Polyethylene (Ex. 30) (b)
-11° C.	33.5	—
0° C.	30.4	120.4
10° C.	26.6	72.3
20° C.	26.1	71.1
30° C.	—	76.0
40° C.	25.5	78.2
50° C.	24.5	—
65° C.	—	84.4
ηf (Kilopoises \times CPS)		
-11° C.	755	—
0° C.	577	4844
10° C.	459	826
20° C.	341	634
30° C.	—	659
40° C.	295	782
50° C.	254	—
65° C.	—	1445
Relative Damping, %		
-11° C.	16.5	—
0° C.	14.1	27.7
10° C.	12.9	8.7
20° C.	9.9	6.9
30° C.	—	6.7
40° C.	8.9	7.7
50° C.	8.0	—
65° C.	—	12.8
Frequencies (CPS)		
-11° C.	3.60	—
0° C.	3.43	5.04
10° C.	3.46	4.60
20° C.	3.42	4.56
30° C.	—	4.57
40° C.	3.38	4.64
50° C.	3.31	—
65° C.	—	4.68

- (a) Cured 30'/307° F. with following recipe:
Rubber, 100; Stearic Acid, 1; Age Rite Stalite, 2; Zinc Oxide, 3; Sulfur, 1.5;
Tetramethylthiuram Disulfide, 0.1; Benzothiazyl Sulfide, 1.
- (b) Cured 20'/280° F. with following recipe:
Rubber, 100; Sulfur, 2; Tetramethylthiuram Disulfide, 1; Benzothiazyl
Sulfide, 1; Zinc Oxide, 5.

The above data in Table X shows that chlorinated polyethylene is stiffer (higher K) and has a higher internal viscosity (η_f) than natural rubber. However, whereas the η_f of natural rubber decreases with increasing temperature, the η_f of chlorinated polyethylene reaches a minimum and then rises with increasing temperature. Within the temperature range 10° to 50° C. the chlorinated polyethylene has a lower relative damp (which means a higher resilience) than natural rubber. The hysteresis properties of chlorinated polyethylene are poorer than those of natural rubber by virtue of the higher internal viscosity (η_f). Thus, this example further illustrates the unusual dynamic properties of chlorinated polyethylenes prepared according to the process of this invention.

WHAT WE CLAIM IS:—

1. The process for preparing an elastomeric halogenated polyethylene comprising the steps of (1) dissolving polyethylene in an inert aromatic diluent, (2) introducing a halogenating agent consisting of or containing chlorine or bromine, into the resultant solution at a temperature in the range 60—170° C. to produce a halogenated polyethylene, containing from 25 to 65 wt. % of halogen, and having sufficient unsaturation to be cured by sulfur, and sufficient halogen so that there is substantially no residual crystallinity.

2. The process of claim 1 wherein the halogenating agent is a brominating agent and

the resulting brominated polyethylene contains from 40 to 60 wt. % of bromine.

3. The process of claim 1 wherein the halogenating agent is a chlorinating agent, and the resulting chlorinated polyethylene contains from 27 to 35 wt. % of chlorine.

4. The process of any of claims 1 to 3 wherein the unsaturation is in the range of 1.0 to 3.0 mole %, calculated as described in relation to Table I.

5. The process of any of claims 1 to 4 wherein the halogenation is carried out at a temperature of from 70 to 120° C.

6. The process of any of claims 1 to 5 wherein the aromatic diluent is benzene, a chlorobenzene or a polychlorobenzene.

7. The process of claim 1 or any of claims 3 to 6 wherein the halogenating agent is dichlorodimethyl hydantoin.

8. The process of claims 1 or 2 or any of claims 4 to 6 wherein the halogenating agent is N-bromo succinimide.

9. The process of preparing an elastomeric halogenated polyethylene as claimed in claim 1, substantially as hereinbefore described in the Examples.

10. An elastomeric chlorinated or brominated polyethylene when prepared according to a process claimed in any of claims 1 to 9.

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